# III.A.25 Low-Cost Integrated Composite Seal for SOFC: Materials and Design Methodologies

## Objectives

- Investigate the effects of the ceramic layer on the chemical stability of the composite seal
- Investigate the mechanical failure and strength of the composite seal

## Accomplishments

- Proved that the ceramic layer in the composite seal effectively isolates the chemical interaction of certain reactive filler glass and stainless steel substrates
- Observed the failure modes and quantified the strength of the composite seal

## Introduction

Previous work [1] reported by the author has demonstrated an integrated composite seal concept for SOFCs. The composite seal samples were fabricated and tested for leak performance at steady state and thermo-cycling conditions. The composite seal sample with one combination of constituents has demonstrated a leak rate of 0.017 sccm/cm (2 psig helium) and survived over 60 thermo-cycles from 150°C to 650°C at 5°C/min.

If placed in direct contact, glass and glass-ceramic materials may chemically interact with Fe-Cr-based stainless steel at high temperature. For example, barium-calcium-aluminosilicate (BCAS) based sealing glasses seem to be susceptible to this form of interactions, especially when used in combination with high-chromium-content stainless steels. Under prolonged exposure to high temperature, the chromium in the steel combines with Barium in the glass to form $BaCrO_4$ at the edges where air is available to supply oxygen [1,2]. In the sample interior, chromium dissolves into the glass to form solid solutions and produce porosity at the interface. Such interactions compromise the hermetic sealing and bonding strength of the seal. In the composite seal concept, an inert ceramic layer is disposed in between the filler (e.g. glass) and the substrate [1]. By eliminating direct contact between the glass and the Fe-Cr alloy, the ceramic layer in the composite seal was expected to help reduce adverse chemical interactions between the glass fillers and the metal substrates, thus improving long-term stability and/or mechanical bonding strength of the seal. And it was the purpose of this work to prove such advantages of the composite seal structure.


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## Approach

Experimental studies were carried out to compare seal samples made with and without the ceramic layer. The stability study utilized metal-glass-metal and metal-ceramic-glass-ceramic-metal sandwich specimens made from Fe-Cr stainless steel with and without a ceramic interlayer. Alloy strips without the ceramic layer were cut into 10 mm x 10 mm squares, then ground and polished using 600-grit SiC paper. The samples were then ultrasonically cleaned in ethanol for 10 minutes and rinsed using acetone to eliminate contamination. A thin layer of G18 sealing glass was applied in the form of green tape. The samples were then transferred to a high temperature oven for curing under a small dead load pressure, approximately 7 kPa. The cured samples were subjected to a constant temperature of 800°C for a week (168 hours) and then cooled down at 1°C/min. After aging, the specimens were mounted in epoxy, sectioned and polished to a surface finish of 1 micron for SEM and electron micro probe analysis. Standard tensile adhesion tests (ASTM C633-01) were conducted on plasma sprayed ceramic coatings to evaluate mechanical pull-out strength of the coating itself and then sandwich samples with a glass interlayer were made and tested in the same pull out setup to gauge bond strength. Samples were bonded with FM1000 epoxy adhesive from Cytec Engineered Materials, Inc. to the pull-out bars, which were connected through two universal joints to an Instron servo hydraulic loading frame. The samples were pulled apart with a cross head speed of 0.015 mm/sec. A minimum of five samples was tested for each material combination.

## Results

For the sample without an atmospheric plasma spray (APS) ceramic buffer layer, the interaction between the Fe-Cr substrate and the G18 glass is apparent. A back scattered electron (BSE) image and electron probe micro analysis (EPMA) elemental mappings after aging are shown in Figure 1. Notably, Cr and Ba inter-diffused and probably formed a reaction layer.

A BSE electron image and EPMA elemental mappings for samples with APS coating after aging are shown in Figure 2. For samples with an APS buffer layer, no trace of chemical interaction between the glass and the Fe-Cr substrate was identified. However, Fe-Ni inter-diffusion occurred between the bond coat of the APS coating and the Fe-Cr substrate.

Tensile adhesion test results, shown in Table 1, show that the APS ceramic layer has significant contribution to the adhesion strength of the glass seal. The average failure stress of the Fe-Cr/G18 increased from 2 MPa to about 17 MPa. This is likely due to the elimination of the weak reaction layer between G18 and the Fe-Cr substrates and better chemical compatibility of the G18 glass and the APS ceramic layer ($Al_2O_3$ and YSZ).

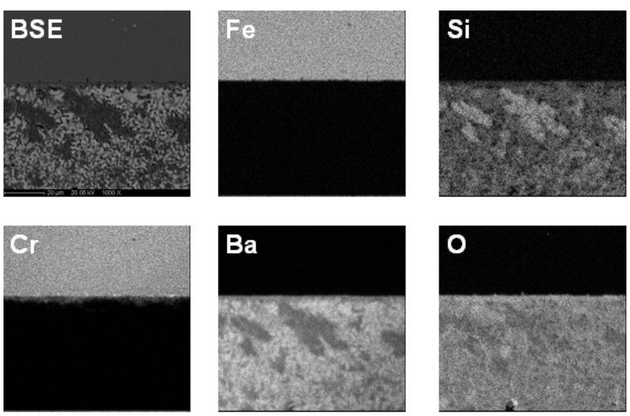


**FIGURE 1.** Scanning Electron Microscopy (SEM) Images of the Cross-Section of Fe-Cr/G18 Sample after High Temperature Aging; BSE Electron Image; Elemental Maps Shown Are Obtained by EPMA

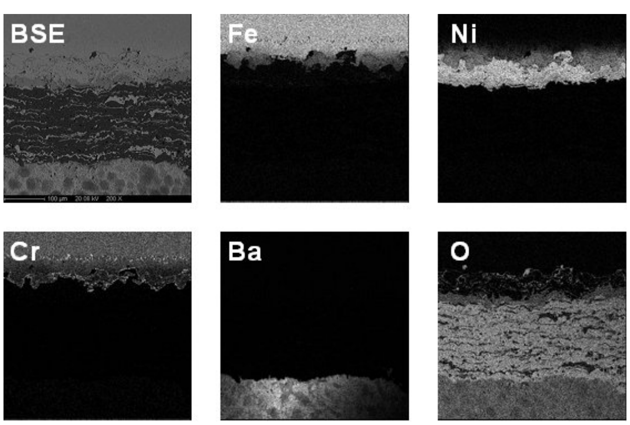


**FIGURE 2.** SEM Images of the Cross-Section of Fe-Cr/APS/G18 Interface after High Temperature Aging; BSE Electron Image; Elemental Maps Shown Are Obtained by EPMA

**TABLE 1.** Tensile Adhesion Test Results

| | APS Coat Only | APS Coat with Glass | No Coat with Glass |
|---|---|---|---|
| Failure Stress (MPa) | 41.52 | 11.27 | 0.35 |
| | 21.88 | 23.50 | 3.26 |
| | 30.19 | 25.90 | *N/A |
| | 34.07 | 12.96 | 2.35 |
| | 27.19 | 11.27 | *N/A |
| Mean | 30.97 | 16.98 | 1.99 |
| Standard Deviation | 7.39 | 7.13 | 1.49 |

* Sample failed during handling

## Conclusions and Future Directions

The work clearly showed the advantages of the composite seal in (1) avoiding adverse chemical interaction between reactive glass and the Fe-Cr stainless substrate and (2) improving the bonding strength due to the ceramic interlayer.

## FY 2006 Publications/Presentations

1. Srivatsan Narasimhan, Xinyu Huang, Serg Timin, Lindsay Wright, Kris Ridgeway, Leon Shaw, Ken Reifsnider, “Effect of Ceramic Coating on Chemical Stability of a Composite Seal for Solid Oxide Fuel Cells,” 2006 TMS Annual Meeting & Exhibition, Session: Interconnection and Sealing in Fuel Cells I, Session Chair(s): Frederick S. Pettit; Lorenz Singheiser; Mach 12~16, San Antonio, TX.

2. Xinyu Huang, Xinqing Ma, Kristoffer Ridgeway, Srivatsan Narasimhan, and Ken Reifsnider, “Application of Plasma Sprayed Coatings in a Novel Integrated Composite Seal for SOFCs” (ID #11683) International Thermal Spray Conference (ITSC) & Exposition May 15-18, 2006 Seattle, WA.

## References

1. X. Huang, “Low-cost integrated composite seal for SOFC: Materials and design methodologies,” Section III.A.18, Office of Fossil Energy Fuel Cell Program, FY 2005 Annual Report.

2. Z. Yang, J.W. Stevenson, K.D. Meinhardt, “Chemical interactions of barium-calcium-aluminosilicate-based sealing glasses with oxidation resistant alloys,” Solid State Ionics 160 (2003) 213.

**3.** V.A.C. Haanappel,V. Shemet, I.C. Vinke, S.M. Gross, T.H. Koppitz, N.H. Menzler, M. Zahid, W.J. Quadakkers, "Evaluation of the suitability of various glass sealant-alloy combinations under SOFC stack conditions," Journal of Materials Science 40 (2005) 1583.